

(19) Japan Patent Office (JP)

(12) Laid-Open Patent Publication (A)

(11) Patent Application Laid-Open No.

Tokkai 2002-114824

(P2002-114824A)

(43) Laid-Open Date: April 16, 2002

(51) Int. Cl. ⁷	Internal Classification	F1	Subject Code (Reference)
C 08 F 214/22		C 08 L 65/00	4F071
216/14		C 08 G 61/08	4J002
C 08 J 5/00		H 01 B 1/24	CEW 4J002
C 08 K 5/00		H 01 M 8/02	
C 08 L 27/16			

Examination Requested: Not requested

Number of Claims: 9 OL (Total 8 pages)

(21) Application No: Tokkai 2000-305071
(P2000-305071)

(22) Date Filed: October 4, 2000

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(54) Title of the invention: Fluorine-containing elastomer

(57) Summary

Subject Matter: To provide a fluorine-containing elastomer and a vulcanizing composition capable of providing a vulcanized material with a low glass transition temperature and particularly excellent cold resistance at the level of -40°C that is useful as a sealing material for use in fuel systems of automobile engines.

Means of Solution: A fluorine-containing elastomer comprising a copolymer composition of 50–85 mol percent vinylidene fluoride and 15–50 mol percent perfluoro(2-methoxypropylvinyl ether), the number-average molecular weight of which is 8000–500000 and the weight-average molecular weight of which is 20000–1000000.

Scope of Patent Claims

Claim 1. A fluorine-containing elastomer comprising a copolymer composition of 50–85 mol percent vinylidene fluoride and 15–50 mol percent perfluoro(2-methoxypropylvinyl ether), the number-average molecular weight of which is 8000–500000 and the weight-average molecular weight of which is 20000–1000000.

Claim 2. A fluorine-containing elastomer comprising a copolymer composition containing 20–85 mol percent vinylidene fluoride, 15–50 mol percent perfluoro(2-methoxypropylvinyl ether), and 50 mol percent or less of at least one of the group formed by tetrafluoroethylene, perfluoro(methylvinyl ether) and ethylene; the number-average molecular weight of which is 8000–500000 and the weight-average molecular weight of which is 20000–1000000.

Claim 3. A fluorine-containing elastomer set forth in Claim 1 or Claim 2 containing 0.005–1.0 weight percent of iodine atoms.

Claim 4. A method for the manufacture of the fluorine-containing elastomer set forth in Claim 1 or Claim 2 characterized by the radical polymerization of vinylidene fluoride and perfluoro(2-methoxypropylvinyl ether), or vinylidene fluoride, perfluoro(2-methoxypropylvinyl ether) and at least one selected from the group formed by tetrafluoroethylene, perfluoro(methylvinyl ether) and ethylene.

Claim 5. A method for the manufacture of the fluorine-containing elastomer set forth in Claim 3 in which the radical polymerization of Claim 4 is carried out in the presence of a diiodine compound.

Claim 6. A method for the manufacture of a fluorine-containing elastomer set forth in Claim 4 or Claim 5 in which radical polymerization is carried out at a polymerization temperature of 40°C or less.

Claim 7. A vulcanizing fluorine-containing elastomer composition in which 0.05–10 parts by weight of an organic peroxide and 0.1–10 parts by weight of a multifunctional unsaturated compound are compounded with respect to 100 parts by weight of the fluorine-containing elastomer set forth in Claim 3.

Claim 8. A vulcanized and molded material obtained by vulcanizing and molding the vulcanizing fluorine-containing elastomer composition set forth in Claim 7.

Claim 9. A vulcanized and molded material set forth in Claim 8 that is a sealing material for the fuel systems of automobile engines.

Detailed Description of the Invention

0001

Technical field to which the invention belongs: The present invention concerns a fluorine-containing elastomer and a vulcanizing composition capable of providing a vulcanized and molded material having cold resistance at the level of -40°C, and furthermore [concerns] a vulcanized and molded material obtained by vulcanizing and molding this vulcanizing

composition that is suitable as a sealing material for fuel systems of automobile engines and a material for seals of all kinds for use in chemical plants.

0002

Previous technology: In automobile engine fuel systems, chemical plants and the like, there are cases requiring motion and operation in temperature environments below -30°C . For example, in automobile engine fuel systems, with the direct injection in the engines of recent years, there have been [systems] developed in which the injection pressure is as high as 10 MPa. In this case, pressure on the sealing materials used in fuel system lines and the like increases, and sealing materials that can resist this high pressure are being developed.

0003 From the standpoint of chemical resistance and heat resistance, fluororubbers (elastomers) are normally used for sealing materials of this type, but because they are, after all, rubbers, their sealing properties are inferior at low temperatures. Accordingly, copolymers of vinylidene fluoride (VdF) and perfluoro(methyvinyl ether) (PMVE), or furthermore [containing] fluorine-containing elastomers copolymerized of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), ethylene and the like are used as fluororubbers with improved low temperature sealing properties (cold resistance) (Tokkai [Japan unexamined patent application publication] no. H8-157539 [1996], Tokkai no. 50-109280 [1975], Tokkai no. H3-52907 [1991], Tokkai no. H3-221510 [1991], Tokkai no. H7-18027 [1995], Tokkai no. H11-35637 [1999], Tokkai no. H11-80271 [1999], etc.). The presence of PMVE causes the glass transition temperature of these fluorine-containing elastomers to decrease, and they have improved cold resistance.

0004 However, VdF-PMVE-based fluorine-containing elastomers display cold resistance of only around -30°C (T_g of -15 to -33°C), and sealing capability adequate for the above very severe low temperature environments cannot necessarily be obtained.

0005 Accordingly, in order to obtain cold resistance in low temperature environments of -40°C or less, in Tokkai no. S64-52733 [1989], for example, trifluorovinylether monomers having perfluoropolyethers as side chains are copolymerized to attain cold resistance of -60°C ($T_g = -38.5$ to -88°C). However, those special monomers have low emulsion polymerizability, and the manufacturing cost of the monomers is also extremely high, so that the elastomers and vulcanized materials obtained are also expensive.

0006 In addition, in Tokkai no. H11-349647 [1999], it is disclosed that fluorine-containing elastomers copolymerized of VdF, TFE and PMVE in the presence of compounds having iodine-containing groups on both ends of perfluoropolyether chains have excellent cold resistance (in TR tests, $TR_{10} = -35$ to -40°C). However, because the iodine-containing perfluoropolyether compounds are expensive and moreover are required in large amounts, the elastomers and vulcanized materials obtained are expensive.

0007 Furthermore, in pamphlet no. WO00/12574, cold-resistant fluorine-containing elastomers ($T_g = -70$ to -119°C) containing (OCF_2) and $(\text{OCF}_2\text{CF}_2)$ units and the like are disclosed, but the manufacturing process for the monomers that provide (OCF_2) and $(\text{OCF}_2\text{CF}_2)$ units is complicated, and this makes the elastomers and vulcanized materials obtained expensive.

0008

Problems the invention attempts to solve: The present invention, as the result of repeated research towards providing fluorine-containing elastomers that can attain cold resistance to the

level of -40°C without decreasing their chemical resistance, at a lower cost than previously, discovered that perfluoro(2-methoxypropylvinyl ether) (PMPVE) can be manufactured by a 3-step synthesis method similar to that for PMVE, and that it moreover has a great effect in reducing Tg, thus completing the present invention.

0009

Means for solution of the problem: Namely, the present invention concerns a fluorine-containing elastomer comprising a copolymer composition of 50–85 mol percent VdF and 15–50 mol percent PMPVE, the number-average molecular weight of which is 8000–500000 and the weight-average molecular weight of which is 20000–1000000.

0010 In addition, it concerns a fluorine-containing elastomer comprising a copolymer composition containing 20–85 mol percent VdF, 15–50 mol percent PMPVE, and 50 mol percent or less of at least one of the group formed by TFE, PMVE and ethylene; the number-average molecular weight of which is 8000–500000 and the weight-average molecular weight of which is 20000–1000000.

0011 Of these fluorine-containing elastomers, those containing, for example, 0.005–1.0 weight percent of iodine atoms as crosslinking sites are preferred as vulcanizable fluorine-containing elastomers.

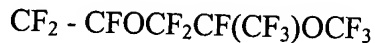
0012 These fluorine-containing elastomers can be manufactured by radical copolymerization, preferably at a polymerization temperature of 40°C or less, of VdF and PMPVE, and in the case of multicomponent copolymers, furthermore [containing] at least one of the group formed by TFE, PMVE and ethylene. If the radical copolymerization is carried out in the presence of diiodine compounds, vulcanizable iodine-containing fluorine-containing elastomers can be manufactured.

0013 In addition, the present invention also concerns a vulcanizing fluorine-containing elastomer composition comprising the aforementioned iodine-containing fluorine-containing elastomers and 0.1–10 PHR (parts by weight with respect to 100 parts by weight of elastomer; same below) of organic peroxide and 0.1–10 PHR of a multifunctional unsaturated compound.

0014 The present invention further concerns a vulcanized and molded material obtained by vulcanizing and molding this vulcanizing fluorine-containing elastomer composition, and in particular, a fuel system sealing material for automobile engines.

0015

Working embodiment of the invention: VdF and PMPVE are essential structural units of the fluorine-containing elastomer of the present invention. PMPVE is a monomer represented by the formula



and it is manufactured by a 3-step process from the raw ingredient COF_2 in the same way as PMVE. Low-cost manufacturing is consequently possible.

0016 The amount of VdF units contained in the case of binary copolymerization is 50–85 mol percent, preferably 55–80 mol percent, and 60–75 mol percent is further preferred. When there are [too] few VdF units, polymerizability tends to be drastically worsened; when there are [too] many, it becomes more difficult to obtain elastomeric properties. The amount of PMPVE units

contained is 15–50 mol percent, preferably 20–45 mol percent, and 25–40 mol percent is further preferred. When there are [too] few PMPVE units, its effectiveness in lowering T_g is reduced, making cold resistance, which is the object [of the invention], inadequate; and when there are [too] many, it becomes more expensive.

0017 The elastomer comprising the VdF–PMPVE two-component copolymer of the present invention has a number-average molecular weight of 8000–500000, preferably 20000–300000, and it has a weight-average molecular weight of 20000–1000000, preferably 40000–600000, measured by GPC.

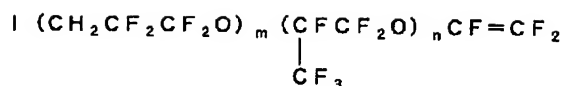
0018 Measurement of average molecular weight by means of GPC is carried out under the following conditions.

GPC:	High-speed GPC apparatus HLC-8020 (manufactured by Tosoh Corporation)
Columns:	Shodex GPC KF 806M (2) (manufactured by Showa Denko K.K.) Shodex GPC KF 800M (1) (manufactured by Showa Denko K.K.)
Detector:	RI detector (differential refractometer)
Expansion solvent:	Tetrahydrofuran
Temperature:	35°C
Concentration:	0.2 weight percent
Standard polystyrene:	Monodisperse polystyrene, all types (M _w /M _n = 1.14 (max.)) TSK standard Polystyrene (manufactured by Tosoh Corporation)

0019 In the present invention, other comonomers may be copolymerized with VdF and PMPVE. Examples of other comonomers include TFE, PMVE and ethylene, and up to 50 mol percent, preferably up to 20 mol percent, particularly 1–15 mol percent may be copolymerized. In that case, the VdF [content] is 20–85 mol percent, preferably 60–80 mol percent, and the PMPVE [content] is 15–50 mol percent, preferably 15–30 mol percent. TFE is particularly preferred as a comonomer, from the standpoints of cold resistance, solvent resistance and the like. The multinary fluorine-containing elastomer of the present invention comprising VdF–MPVE–other comonomer has a number-average molecular weight of 8000–500000, preferably 20000–300000, and a weight-average molecular weight of 20000–1000000, preferably 40000–600000, measured by GPC.

0020 Furthermore, if required, functional group-containing monomers that supply units providing crosslinking sites may be copolymerized. Examples of functional group-containing comonomers include iodine-containing monomers, bromine-containing monomers, monomers containing nitrile groups and 2–hydropentafluoropropene. Among these, iodine-containing monomers, particularly iodine-containing fluoromonomers, are appropriate. As specific examples, monomers shown by the formula set forth in Tokkai no. H8-157539 [1996]:

0021

Chemical structure 1

0022 (in the formula, m is an integer from 1 to 5, n is an integer from 0 to 3), or the iodine-containing monomers represented by $\text{CH}_2=\text{CH}(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{I}$ (see Tokkai no. H7-316234 [1995]) are preferred. Their copolymerization fraction is 3 mol percent or less, preferably 0.005–1.5 mol percent.

0023 Crosslinking sites may also be introduced into the fluorine-containing elastomer of the present invention by means of radical copolymerization of the above monomers in the presence of a diiodine compound, so that vulcanization can be endowed. The amount of iodine introduced into the copolymer by means of the diiodine compound is preferably 0.05–1.0 weight percent with respect to the total elastomer weight (calculated from the weight of diiodine compound added during polymerization). As for the amount of diiodine compound present in the elastomer, as stated in Tokkai no. S53-125491, because the diiodine compound acts as chain transfer agent, [the amount] has an important meaning for the determination of molecular weight, and the iodine introduced also functions as crosslinking sites. Consequently, when the amount of iodine is less than 0.05 weight percent of the elastomer weight, the molecular weight of the elastomer obtained becomes too large, and fluidity lost during vulcanization results in reduced crosslinking density, and the molded material does not display sufficient tear strength. In addition, when it exceeds 1.0 weight percent, the molecular weight becomes too low, and this impedes the rubber kneading operation.

0024 Representative examples of these diiodine compounds include 1,3-diiodoperfluoropropane, 1,4-diiodoperfluorobutane, 1,3-diiodo-2-chloro-perfluoropropane, 1,5-diiodo-2,4-dichloroperfluoropentane, 1,6-diiodoperfluorohexane, 1,8-diiodoperfluorooctane, 1,12-diiodoperfluorododecane and 1,16-diiodoperfluorohexadecane, diiodomethane and 1,2-diiodoethane; and these may be used singly, or they can be used together in combination. Preferred diiodine compounds include 1,4-diiodoperfluorobutane.

0025 The elastomer of the present invention can be manufactured by carrying out radical emulsion copolymerization of VdF, PMPVE, and furthermore, if required, TFE, PMVE [and/or] ethylene, or furthermore an iodine-containing fluorinated vinyl ether during agitation under pressure, for example essentially in the absence of oxygen in aqueous solvent, and if required, in the presence of a diiodine compound.

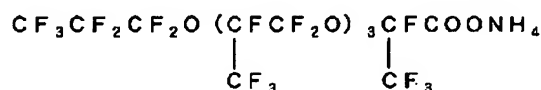
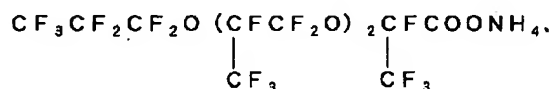
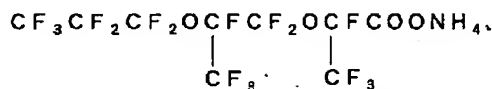
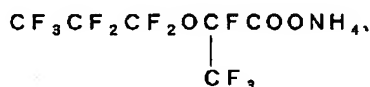
0026 Radical polymerization initiators previously used in the polymerization of fluorine-containing elastomers can be used in the radical polymerization. These initiators include organic and inorganic peroxides, and azo compounds. Typical initiators include persulfate salts, peroxycarbonates and peroxyesters, and preferred initiators include ammonium persulfate (APS). APS can be used alone, or it can also be used in combination with reducing agents such as sulfites and sulfurous acid salts. As for the amount of initiator added during polymerization, from the standpoint of the physical properties of the elastomer produced (for example, compression set, tensile strength, etc.), as little as possible is preferred. However, [the use of] markedly small amounts, by reducing the polymerization speed, can be a major factor in worsening productivity,

and adjustment is necessary. Normally, 0.05–0.5 mol is used with respect to 1 mol of diiodine compound.

0027 The radical polymerization in the present invention can be implemented by methods such as suspension polymerization, emulsion polymerization and solution polymerization, but implementation by means of suspension polymerization or emulsion polymerization is particularly preferred. In the case of emulsion polymerization, a wide range of emulsifying agents can be used. Carboxylic acid salts having fluorocarbon chains or fluoropolyether chains are particularly desirable from the viewpoint of suppressing chain transfer reactions to the emulsifying agent occurring during polymerization. Specific examples of emulsifying agents include:

0028

Chemical structure 2



0029 The amount of emulsifying agent used is preferably approximately 0.05–10 weight percent of the water added, and 0.1–1.0 weight percent is particularly preferred.

0030 In addition, to aid in the emulsification of PMPVE, fluorine-containing alcohols such as pentafluoropropanol, 2,2,3,3,3-pentafluoropropanol and 2,2,3,3-tetrafluoropropanol may be added as auxiliary agents; and high pressure homogenizers such as the Microfluidize M-210E/model H made by Microfluidize International and the Gorin Homogenizer made by Nippon Seiki Seisakusho K.K.¹ can be used to forcibly emulsify it.

0031 A polymerization temperature of 40°C or less is preferred. When it is higher than 40°C, the product obtained has a low molecular weight, and it may present as a liquid or the like, making it impossible to obtain elastomeric properties. [The temperature] is specifically determined by the type of initiator used and the presence or absence of a reducing agent. In general, a temperature

¹ Unable to confirm official English product or company name.

of 0–40°C is employed, but if APS and sodium sulfite are used as the polymerization initiator, a temperature of 5–30°C is preferred.

0032 A wide range of polymerization pressures can be employed, but in general, 10 MPa or less, preferably 2 MPa or less, is employed. Because the higher the polymerization pressure the greater the polymerization speed, 1.0 MPa or higher is desirable from the viewpoint of increasing productivity. However, to increase the amount of PMPVE, which is a liquid monomer, that is copolymerized, the low pressure region (0.2–1.0 MPa) is preferred.

0033 The polymerization time differs according to the types of monomers copolymerized, but 3–50 hours is appropriate from the viewpoint of productivity.

0034 After polymerization is completed, the elastomer is recovered, according to the method specified, after undergoing coagulation and drying processes. At this time, vacuum drying treatment may be carried out in order to recover unreacted PMPVE, which is more expensive than the other monomers.

0035 The vulcanizable fluorine-containing elastomer of the present invention thus obtained can be crosslinked by means of a variety of crosslinking agents and cured (vulcanized) to make a vulcanized material. High energy electromagnetic waves such as radiation (α rays, β rays, γ rays, electron waves, X-rays, etc.) can also be used as crosslinking agents, but organic peroxides are preferably used.

0036 Consequently, the present invention also concerns a vulcanizing composition comprising the aforementioned novel vulcanizable fluorine-containing elastomer and an organic peroxide and a multifunctional unsaturated compound.

0037 As an organic peroxide, in general, one that gives off peroxy radicals easily in the presence of heat or an oxidation-reduction system is preferred, and examples include 1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane, 2,5-dimethylhexane-2,5-dihydroperoxide, di-t-butylperoxide, t-butylcumylperoxide, dikumylperoxide², α , α -bis(t-butylperoxy)-p-diisopropylbenzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-di-methyl-2,5-di(t-butylperoxy)-hexane-3, benzoylperoxide, t-butylperoxybenzene, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, t-butylperoxy maleic acid and t-butylperoxyisopropylcarbonate. Dialkyl-type [compounds] are particularly preferred. Among those, 2,5-dimethyl-2,5-di(tertiary butylperoxy)hexane is particularly preferred. In general, the type of organic peroxide and the amount used are selected taking into consideration the amount of active –O–O–, the decomposition temperature, and the like. The amount used is 0.05–10 PHR, preferably 0.1–10 PHR, and more preferably 1.0–5 PHR.

0038 In addition, when an organic peroxide is used, suitable vulcanization can be implemented by using it together with a multifunctional unsaturated compound as a crosslinking accelerator. If this multifunctional unsaturated compound has reaction activity with respect to the peroxy radicals and the polymer radicals, then it is effective in principle, and the type [of compound] is not particularly restricted. Preferred [compounds] include triallyl cyanurate, triallyl isocyanurate, triacrylformal, triallyl trimellitate, N,N'-m-phenylenebismaleimide, dipropargyl terephthalate, diallyl phthalate, tetraallyl terephthalate amide, triallyl phosphate, and bis-olefins represented by $\text{CH}_2=\text{CH}(\text{CF}_2)_6\text{CH}=\text{CH}_2$ (see Tokkai no. H9-124870 [1997]). Among those, triallyl

² Comma added, run on in original.

isocyanurate is particularly preferred. The amount used is preferably 0.1–10 PHR, more preferably 0.5–5 PHR.

0039 Additives in general use may be suitably added to the vulcanizing composition of the present invention. Those additives include fillers, reinforcing materials, pigments and process assisting agents. Fillers and reinforcing agents that are commonly used include inorganic ones such as carbon black, TiO_2 , SiO_2 , clay and talc; and among the organic ones, fluorine-containing polymers such as polytetrafluoroethylene, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, tetrafluoroethylene/ethylene copolymers and tetrafluoroethylene/vinylidene fluoride copolymers.

0040 In addition, other rubbers and the like may be compounded together and covulcanized. Rubbers of this kind include silicone oil, silicone rubber, ethylene/vinyl acetate copolymer, 1,2-polybutadiene, fluorosilicone oil, fluorosilicone rubber, fluorophosphazene rubber, hexafluoropropylene/ethylene copolymer and tetrafluoroethylene/propylene copolymer, and furthermore, other polymers with radical reactivity can be used. The amount of these used is not particularly restricted, but when cold resistance is the objective, they should naturally not be [used] to the extent that they impair the cold resistance.

0041 Conventional peroxide vulcanizing methods may be used as the vulcanization method. An example is a method in which press vulcanization is carried out on unvulcanized material that has been, for example, kneaded in oven rolls or a powder mixer, or dissolved or dispersed in a solvent to make a dispersion mixture, normally at a temperature of 120–200°C for 5–30 minutes, and then oven vulcanization is carried out at 150–250°C for 1–24 hours.

0042 The present invention further concerns a vulcanized material. The vulcanized material of the present invention has a low T_g of -45°C to -30°C, and is an elastomer vulcanized material with particularly excellent cold resistance. Consequently, the vulcanized material of the present invention can of course be used as general-purpose molding materials, sealants, paints and the like requiring heat resistance, oil resistance, chemical resistance, solvent resistance and the like, but in particular, it can provide sealing materials for automobile engine systems that require cold resistance to a level of -40°C, at relatively low cost. As a sealing material, its particularly preferred embodiments include O-rings, lip-type packings, oil seals, gaskets and V-rings. In addition, it is useful as a sealing material in chemical plants, manufacturing apparatus of all types and analysis apparatus that operate at low temperatures.

0043

Working examples: Next, the present invention is explained in further detail by means of working examples, but the present invention is not limited only to these working examples.

0044 Working Example 1

5.0 g of PMPVE, 25 g of 1,1-dichloro-1-fluoroethane (HCFC-141b), and 2.8 g of bis(2,4,5-trichloroperfluorohexanoyl)peroxide (DLP) in perfluorohexane solution (concentration 20 weight percent) were put into an autoclave made of stainless steel 316 with an inside volume of 123 ml (actual volume); and after cooling with dry ice/acetone liquid, the inside of the system was replaced with nitrogen. After the pressure was reduced to a vacuum, 3.9 g of VdF were added, and the reaction was carried out at 20°C while shaking. As the reaction proceeded, the pressure (gauge pressure) inside the system was reduced from 0.50 MPa to 0.40 MPa 55 minutes later. At this point, the unreacted monomers were released, and the reaction product was vacuum

dried at 80°C until it reached a constant weight, to obtain 2.8 g of the fluorine-containing elastomer of the present invention.

0045 When this elastomer was analyzed by ^{19}F -NMR, the monomer unit composition was 80.5 mol percent VdF and 19.5 mol percent PMPVE. The number-average molecular weight was 9700, and the weight-average molecular weight was 36300, measured by GPC. In addition, T_g , measured by a differential calorimeter (DSC), was -37°C.

0046 Working Example 2

A fluorine-containing elastomer of the present invention was manufactured in the same way as in Working Example 1, except that the polymerization conditions and the starting monomer composition shown in Table 1 were employed. The physical properties of the fluorine-containing elastomer obtained are shown in Table 1.

0047

Table 1

	Table 1	
	Working Example	
	1	2
Starting amount of DLP solution (g)	2.8	2.2
Starting amount of monomers		
VdF/PMPVE (g)	3.9/5.0	1.8/9.3
(mol % ratio)	80.2/19.8	49.6/50.4
Time shaken (minutes)	55	60
Pressure change	0.50→0.40	0.24→0.16
Amount of elastomer obtained (g)	2.8	3.1
Elastomer composition		
VdF/PMPVE (mol percent ratio)	80.5/19.5	65.2/34.8
T_g (°C)	-37	-32
Average molecular weight		
M_n ($\times 10^4$)	0.97	0.69
M_w ($\times 10^4$)	3.63	0.96
M_w/M_n	3.73	1.40

0048 Working Example 3

3.0 g of PMPVE, 25 g of HCFC-141b and 1.9 g of DLP in perfluorohexane solution (concentration 20 weight percent) were put into an autoclave made of stainless steel 316 with an inside volume of 123 ml (actual volume); and after cooling with dry ice/acetone liquid, the inside

of the system was replaced with nitrogen. After the pressure was reduced to a vacuum, 2.5 g of VdF and 0.2 g of TFE were added, and the reaction was carried out at 20°C while shaking. As the reaction proceeded, the pressure (gauge pressure) inside the system was reduced from 0.38 MPa to 0.36 MPa 22 minutes later. At this point, the unreacted monomers were released, and the reaction product was vacuum dried at 80°C until it reached a constant weight, to obtain 0.6 g of the fluorine-containing elastomer of the present invention.

0049 When this elastomer was analyzed by ^1H -NMR and ^{19}F -NMR, the monomer unit composition was 67.6 mol percent VdF / 11.8 mol percent TFE / 20.6 mol percent PMPVE. The number-average molecular weight was 9200, and the weight-average molecular weight was 28800, measured by GPC. In addition, T_g , measured by a differential calorimeter (DSC), was -40°C.

0050 Working Examples 4-6

Fluorine-containing elastomers of the present invention were manufactured in the same way as in Working Example 3, except that the polymerization conditions and the starting monomer compositions shown in Table 2 were employed. The physical properties of the fluorine-containing elastomers obtained are shown in Table 2.

0051 Although the copolymers are combinations of the same copolymerized monomers, the glass transition point varies according to the copolymer fraction of VdF. Because of that, [the results] show glass transition points ranging from around -45 to -30°C. Working Example 4 shows a relatively high glass transition point of -30°C, but because the copolymer fraction of VdF is relatively low and the copolymer fraction of TFE is high, it is a polymer characterized by excellent solvent resistance. In this range of copolymer fractions, the respective glass transition points are around 10°C lower than when PMVE, which is the previous technology, is used.

0052

Table 2

Table 2

	Working Example			
	3	4	5	6
Starting amount of DLP (g)	1.9	2.8	2.1	2.1
Starting amount of monomers				
VdF/TFE/PMPVE (g)	2.5/0.2/3.0	4.0/0.9/3.0	3.0/0.2/3.0	2.5/0.2/6.0
(mol % ratio)	78.0/4.0/18.0	77.6/11.2/11.2	80.9/3.5/15.6	66.0/3.4/30.6
Time shaken (minutes)	22	37	15	22
Pressure change	0.38→0.36	0.61→0.52	0.34→0.32	0.42→0.40
Amount of elastomer obtained (g)	0.6	2.4	0.8	1.3
Elastomer composition				
VdF/TFE/PMPVE	67.6/11.8/20.6	66.4/27.0/6.6	71.1/12.6/16.3	61.5/18.4/20.1
(mol % ratio)				
Tg (°C)	-40	-30	-36	-40
Average molecular weight				
Mn (x10 ⁴)	0.92	3.36	1.53	2.48
Mw (x10 ⁴)	2.88	6.64	3.23	4.95
Mw/Mn	3.13	1.98	2.11	2

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Effectiveness of the invention: The fluorine-containing elastomer of the present invention provides a vulcanized material with a low Tg and particularly excellent cold resistance to a level of -40°C. This vulcanized material is useful as a sealing material for use in the fuel systems of automobile engines.

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F-terms (reference): 4F071 AA26 AA81 AA86 AH03 AH19
BC07
4J002 BD141 BE041 EA018 EB006
EH148 EK037 EK047 EK057
EK087 EP008 ER008 EW048
FD156 FD158 GJ02 GN00
4J100 AA02R AC24P AC26R AE09Q
AE09R BA02Q BB07Q BB07R
BB13Q BB18Q BB18R CA04
CA05 DA01 JA28

